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Vapour-phase gold-surface-mediated coupling of aldehydes with methanol

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Selective coupling of oxygenates is critical to many synthetic processes, including those necessary for the development of alternative fuels. We report a general process for selective coupling of aldehydes and methanol as a route to ester synthesis. All steps are mediated by oxygen-covered metallic gold nanoparticles on Au(111). Remarkably, cross-coupling of methanol with formaldehyde, acetaldehyde, benzaldehyde and benzeneacetaldehyde to methyl esters is promoted by oxygen-covered Au(111) below room temperature with high selectivity. The high selectivity is attributed to the ease of nucleophilic attack of the aldehydes by the methoxy intermediate—formed from methanol on the surface—which yields the methyl esters. The competing combustion occurs via attack of both methanol and the aldehydes by oxygen. The mechanistic model constructed in this study provides insight into factors that control selectivity and clearly elucidates the crucial role of Au nanoparticles as active species in the catalytic oxidation of alcohols, even in solution.

Gold-based catalysts have been the subject of intense study over the past decade because of the promise of selective and energy-efficient oxidation processes. Recently, there has been a focus on selective oxidation of alcohols[1–19], due in part to interest in biomass conversion to fuels and useful synthetic chemicals, such as esters and organic acids. There is a specific interest in replacing current technology for stoichiometric oxidation of alcohols[20] with a catalytic process that could reduce energy consumption, increase selectivity and minimize production of environmental pollutants. Gold-based catalysts have, in particular, shown promise for efficient and selective oxidative coupling of alcohols[7].

A critical goal of catalytic research in alcohol oxidation is the construction of a predictive model that guides the design of processes and materials in order to enhance selectivity for specific processes. Herein, we describe investigations of complex cross-coupling reactions in order to provide a roadmap for controlling selectivity using Au catalysts. We further demonstrate that all steps in these oxidative cross-coupling reactions can be mediated by oxygen-covered Au nanoparticles in the absence of a metal oxide support. Previously, several mechanisms proposed for liquid-phase oxidative coupling invoked a combination of reactions on the supported Au catalyst and in the liquid phase[2,5,7,13–16]. Our work shows that solution-phase reactions are not necessary. We also elucidate the elementary molecular transformations that are important in the coupling reactions, enabling us to qualitatively predict the factors that control selectivity and activity and to extend these reactions to selective cross-coupling.

Model studies of oxidation reactions over coinage metal single-crystal surfaces (Cu, Ag, and Au) have provided insight into the mechanism of catalytic reactions[6,21–25], in some cases leading to predictive microkinetic models[21]. Generally, atomic oxygen bound to coinage metals promotes Brønsted acid–base reactions with protons on reactant molecules, providing a general framework for understanding and predicting reaction pathways[26]. Model studies of vapour-phase reactions induced by oxidized Au are particularly relevant to higher pressure and even aqueous conditions[8,11,27–29] because of several key features: (1) alcohols and other hydrocarbons are only activated when oxygen is present on the Au; (2) water binds only weakly to Au; (3) OH is not thermodynamically stable with respect to disproportionation; and, (4) the dissociation probability for O_2 is extremely low on Au. Therefore, the surface coverages of reactants are low under steady-state conditions. All of these features render the oxidation of alcohols an ideal candidate for linking model studies with working catalytic processes.

Herein, we demonstrate that cross-coupling of aldehydes with methanol is promoted by atomic oxygen bound to Au nanoparticles[30] formed on Au(111), referred to as O/Au(111). The intermediate, methoxy, is first formed from reaction of methanol with oxygen on O/Au(111), as established previously[17]. Cross-coupling between methoxy and four different aldehydes—formaldehyde, acetaldehyde, benzaldehyde and benzeneacetaldehyde—to selectively form the respective methyl esters was observed in our experiments (Fig. 1a). In each case, methoxy was synthesized first by exposing oxidized Au(111) (surface concentration, $\theta_O \approx 0.05$ monolayer) to methanol (0.6 Langmuir) at 140 K, using a protocol established in prior work[17]. Subsequently, the aldehyde was exposed to the surface, followed by heating to promote evolution of products. Reaction selectivities, the nature of the rate-determining step and estimates of the corresponding activation barriers are derived from these experiments. The products were all identified by the observation of their parent ions and by quantitative analysis of their fragmentation patterns (Figs 1 and 2; Supplementary Tables S1 and S2). These results unequivocally demonstrate that methoxy and aldehydes react via a surface-mediated process to yield the corresponding methyl esters. In no case was self-coupling of methanol to methyl formate detected, demonstrating the high selectivity for cross-coupling and the facility of the attack of the aldehydes by methoxy.

Clear evidence for a kinetic predominance of cross-coupling with the aldehydes over self-coupling of the methoxy is derived from isotopic labelling studies in which high selectivity was measured for the reaction $D_2C{=}O + CH_3OH \rightarrow DCOOCH_3$.

We find that deuterium is selectively removed from $D_2C{=}O$ in the reaction of $D_2C{=}O$ and CH_3OH (Supplementary Fig. S3). There is no methyl formate-d_0 detected, which would arise from self-coupling of methanol. This clearly indicates that in the presence

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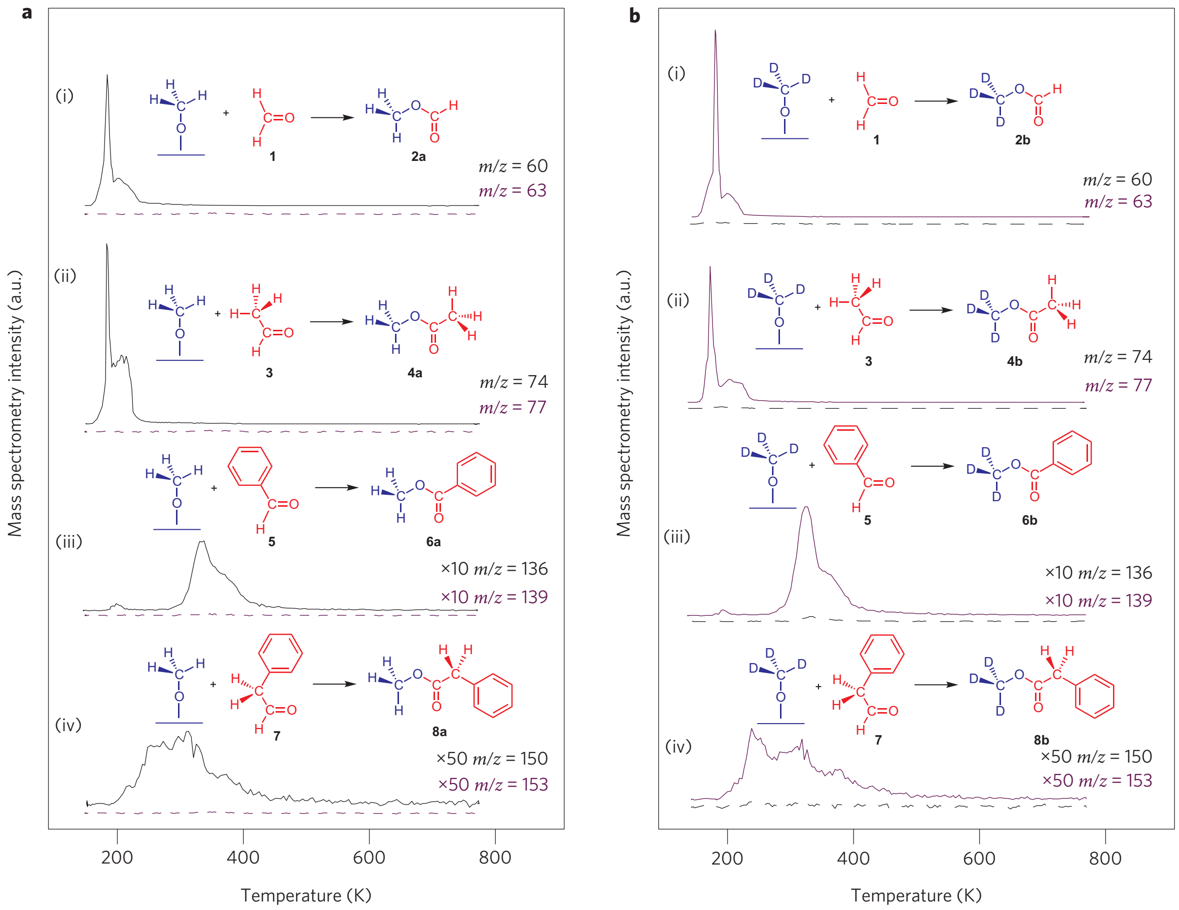

Figure 1 | Mass spectrometric studies of the cross-coupling of isotopically labelled methanol with four different aldehydes. a, Coupling of methoxy-d$_0$ with (i) formaldehyde, (ii) acetaldehyde, (iii) benzaldehyde and (iv) benzeneacetaldehyde. **b**, Coupling of methoxy-d$_3$ with the same four aldehydes. In each case the solid line gives the intensity for the m/z ratio of the expected product assuming no loss of isotopic purity, and the dashed line gives the intensity for the m/z ratio if isotopic purity is lost. The initial oxygen concentration was ~0.05 monolayers in all cases.

of formaldehyde, nucleophilic attack of formaldehyde-d$_2$ is kinetically preferred over β-H elimination of methoxy, as shown in the mechanism constructed from our data (Fig. 2). Isotopic labelling experiments also establish that the methoxy group is preserved in the reaction with the aldehydes and that hydrogen is lost from the aldehydic carbon to yield the esters. The reactions observed are all exclusively $CD_3O_{(ads)} + RC(H){=}O \rightarrow CD_3OC(R){=}O$ (R=H-, CH_3-, Ph-, $PhCH_2$-) (Fig. 1b).

Remarkably, the O/Au(111) promotes ester synthesis with fast kinetics, as signified by the low temperature for ester evolution, which corresponds to an estimated activation barrier of ~8 kcal mol^{-1}. The coupling of methoxy with either formaldehyde or acetaldehyde yields the corresponding gaseous ester in two distinct kinetic processes—that is, in two peaks (Fig. 1). The predominant, lower-temperature process occurs far below room temperature, at 180 ± 5 K, ~40 K lower than the peak temperature measured for self-coupling of methanol and ethanol[17,18]. This is a clear manifestation that the presence of the aldehyde accelerates the formation of the ester by the mechanism illustrated in Fig. 2. By supplying either formaldehyde or acetaldehyde, the rate-limiting step in self-coupling[17,18,31] is circumvented, leading to ester formation at a lower temperature in a process limited by the attack of the aldehyde by the methoxy (Fig. 2).

The nature of the rate-determining step for ester evolution depends on the molecular structure, leading to a higher activation barrier for evolution of the methyl esters containing phenyl rings (benzaldehyde and benzeneacetaldehyde), estimated to be on the order of 15 kcal mol^{-1}. Whereas the production rates of the methyl esters derived from formaldehyde or acetaldehyde are limited by their attack by methoxy, the rates of the methyl esters derived from benzaldehyde and benzeneacetaldehyde are limited by their desorption from the surface (Supplementary Fig. S4). Reactions of methoxy with benzaldehyde and benzeneacetaldehyde yield methyl esters at higher temperature, ~325 K, indicating that the phenyl ring increases the interaction energy of the ester with the surface. Therefore, the phenyl-containing methyl esters will have a longer surface lifetime under steady-state reaction conditions, which could lead to more secondary oxidation if there is oxygen available for reaction.

Surprisingly, the presence of excess aldehyde impedes secondary oxidation to carboxylate species under the conditions of our experiments, where oxygen is in limited supply. There is only a small amount of secondary oxidation to organic acids (<5% relative to the esters) in all cases studied. Carboxylate species were identified as the intermediates leading to secondary oxidation of both methanol and ethanol on O/Au(111) using vibrational spectroscopy[17,18]. In the cases of methanol cross-coupling with formaldehyde, acetaldehyde and benzaldehyde, the corresponding acids—formic acid, acetic acid and benzoic acid—were observed. Both benzoic acid and benzeneacetic acid were detected when methanol cross-coupled with benzeneacetaldehyde (data not shown).

Even though secondary oxidation of the aldehydes themselves occurs if they are reacted in the absence of methoxy on the O/Au(111), the amount of combustion is essentially the same for

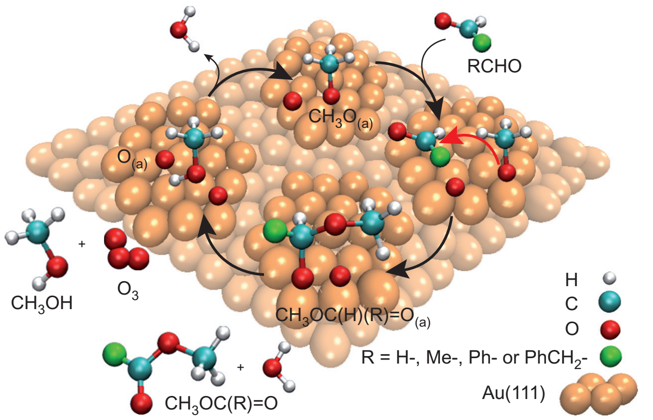

Figure 2 | Schematic mechanism for coupling of methanol and aldehydes on oxygen-covered gold particles. Starting from the left-hand-side, the reaction steps depicted in the figure are: first, O_3 and CH_3OH are introduced sequentially onto the Au(111) surface to form atomic oxygen ($O_{(a)}$) and methoxy ($CH_3O_{(a)}$); next, the aldehyde (RCHO) is introduced, after which nucleophilic attack of methoxy to the aldehydic carbon forms the surface intermediate $CH_3OC(H)(R){=}O_{(a)}$ (the red arrow represents the nucleophilic attack); and last, further β-H elimination of $CH_3OC(H)(R){=}O_{(a)}$ forms the ester ($CH_3OC(R){=}O$).

the reaction of methanol alone (self-coupling) or when there is excess formaldehyde present. As a result, the selectivity, as judged from the ratio of the yields of CO_2 and methyl formate, is increased by a factor of approximately seven relative to the oxidation of methanol alone (Fig. 3). This indicates that the attack of alkoxy to aldehydes competes favourably with that of surface oxygen species in the combustion process. Therefore the cross-coupling reactions effectively suppress the secondary oxidation of aldehydes by directing them to the more facile esterification process.

In all cases studied, the selectivity for esterification relative to combustion is higher when aldehydes are available to react with methoxy on the surface (Fig. 3), clearly demonstrating that attack of the aldehyde by methoxy competes effectively with attack by adsorbed oxygen. The selectivity for ester production relative to combustion to CO_2 on a per molecule basis is ~7:1 and is essentially independent of the molecular structure of the aldehyde (Fig. 3). It is important to note that all oxygen is consumed during the reaction, so it is a limiting reagent. We oxidized the excess carbon deposited from decomposition of secondary oxidation intermediates in the benzaldehyde and benzeneacetaldehyde to estimate the total CO_2 in Fig. 3. The nearly constant CO_2:ester ratio provides an approximate carbon and hydrogen mass balance and shows that there are no major products missing, a point also established in the mass spectrometer analysis. These results are clear evidence that attack by methoxy is more facile than attack by oxygen—leading to combustion—in the case of all four aldehydes, which each have quite different molecular structures.

Our studies clearly show that atomic oxygen present on Au nanoparticles formed on Au(111) promotes cross-coupling of methanol and a variety of aldehydes to selectively yield the corresponding esters. Thus, we unequivocally establish that all steps in the esterification can be mediated by the Au surface and that liquid-phase reactions, including those involving dissolved Au ions, are not necessary. In the liquid phase, alcohols have been selectively and catalytically oxidized to esters[2,5,7–10,19], aldehydes[1–4,6,8,9,11,12] and organic acids[8,12] over Au nanoparticles supported on metal oxides. Our results parallel the addition of aldehydes to methanol catalysed by supported Au in solution, which yielded various methyl esters[7,13,14,16,19].

In our surface-mediated mechanism, an alkoxy hemiacetal ($CH_3OC(H)(R){=}O$) intermediate is proposed to form on the surface during methanol oxidation on O/Au(111)[17] (Fig. 2). Subsequent and rapid loss of hydrogen from the aldehydic carbon yields the ester. This last step may be promoted by adsorbed atomic oxygen or other Brønsted base sites on Au. Our mechanism is in broad agreement with work published previously on supported catalysts, which invokes a qualitatively similar process but without elementary steps[10]. A similar mechanism was previously suggested for methanol self-esterification over O/Ag(110)[25].

In liquid-phase reactions, the initial formation of aldehydes and the final production of the ester were proposed to occur on Au; however, the coupling step was proposed to occur via an acid-catalysed reaction of alcohol and the aldehyde[5,7,13,14]. Surprisingly, the liquid-phase mechanism suggests that the Au catalyst plays no role in these intermediate steps. The fact that all products—including esters—are formed on O/Au(111) is incontrovertible evidence that steps subsequent to aldehyde formation are also promoted on the O/Au surface. Our proposed mechanism provides a guiding principle that esterification involves surface-mediated nucleophilic attack of the aldehydic carbon by alkoxide. Although it is difficult to prove, it is likely that Au-mediated coupling also occurs in solution given the correspondence with our results.

There are several possible roles that the metal oxide support may also play in the liquid-phase reactions. Small amounts of base—for example, Na-methanolate[16] or Lewis acidic supports such as Ga_2O_3 (ref. 10)—enhance the catalytic activity, which might indicate promotion of one or both C–H scission steps by the support. However, the observation of these same steps in vapour-phase reactions with no support indicates that oxygen-covered Au is itself capable of promoting these reactions, most likely through oxygen-assisted C–H bond scission. On Au(111), the protons lost in the overall oxidation of the aldehyde to the ester leave the surface as water. A possible role of the reducible metal oxide support is to serve as a source of adsorbed oxygen on the Au particles. Oxygen is necessary to activate the alcohol and to form the aldehyde in self-coupling. The reducible supports could supply oxygen via spill-over, as has been suggested previously[15] for glucose oxidation over Au supported on CeO_2. A similar concept also applies to reducible oxide-supported Au-particle catalysts: the oxygen atoms at the

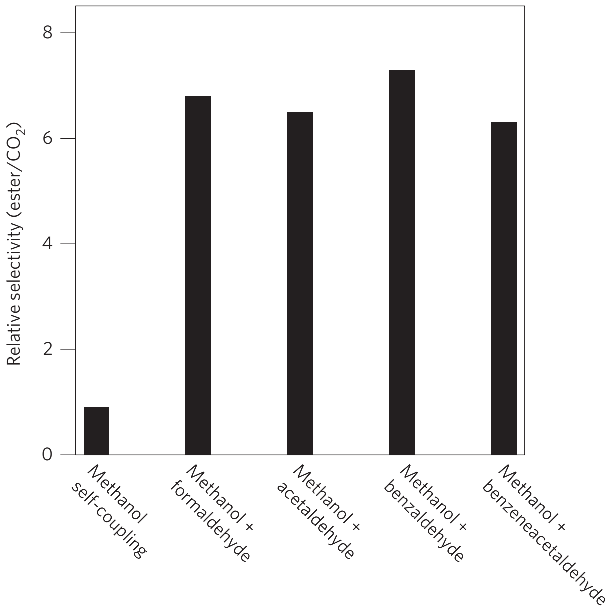

Figure 3 | Relative selectivity of esterification versus combustion in the self-coupling of methanol and cross-coupling between methanol and aldehydes. The selectivity towards esterification is about seven times higher in cross-coupling reactions, compared with that of self-coupling of methanol.

interface between the reducible oxide support and the Au particles could play a very similar role to surface oxygen under ultrahigh vacuum conditions.

In summary, the reactions we observe in our model system—Au nanoparticles covered with atomic oxygen and formed on Au(111)—yield products that closely resemble those for cross-coupling of aldehydes with methanol catalysed by Au nanoparticles in liquid-phase and under aerobic conditions. Importantly, we have demonstrated that this class of reactions occurs when only gaseous components are present, which clearly shows that the O/Au surface plays a pivotal role in all steps in the esterification. Furthermore, we show that this class of reactions occurs in the absence of a metal oxide support, as long as atomic oxygen is present on Au. This suggests that the support may play the important role of supplying oxygen to the Au catalyst[15].

The series of cross-coupling reactions between methanol and four different aldehydes—formaldehyde, acetaldehyde, benzaldehyde and benzeneacetaldehyde—on O/Au(111) in ultrahigh vacuum show the value of molecular-level understanding of the reaction mechanism based on surface chemistry methods. The nucleophilic attack of the aldehydes by methoxy provides a general mechanistic framework for predicting synthetic pathways and for controlling reaction selectivity.

Methods

Experimental setup, surface cleaning and reactant dosing. All experiments were performed in an ultrahigh vacuum chamber with a base pressure below 2×10^{-10} torr. The preparation of the clean Au(111) surface is described elsewhere[30]. The surface was first populated with a 0.05 monolayer of O by introducing an appropriate amount of ozone (O/Au(111)) at 200 K. The oxygen atom coverage was calibrated by comparing the amount of O_2 evolution in a temperature-programmed reaction to that formed for a saturation coverage of oxygen atoms, which is 1.1 monolayers[32]. A $\pm$15% error in oxygen coverage on the Au(111) surface is expected owing to day-to-day variation in O_3 concentration. Oxidation of the surface in this manner leads to release of Au atoms to form nanostructures containing Au and O, most of which are smaller than 2 nm in diameter[30]. We refer to the oxygen-covered Au nanoparticles on Au(111) as O/Au(111).

Methanol and the various aldehydes were sequentially introduced to the O/Au(111) ($\theta_O \approx 0.05$ monolayers) at 140 K. Exposures, corrected for dosing enhancement, are given here in terms of Langmuir, in which 1 Langmuir corresponds to the equivalent of a dose of 1×10^{-6} torr-seconds. Note that this exposure does not take into consideration relative cracking efficiencies in the ion gauge or possible errors due to adsorption, reaction or displacement at chamber walls. Temperature programmed reaction studies were conducted according to well-established protocols[30]. Paraformaldehyde was used as the formaldehyde source and was introduced to the system following the procedure described in the literature[33].

Temperature-programmed reaction spectroscopy. The heating rate for all temperature-programmed experiments was nearly constant at $\sim 5 \pm 0.5$ K s^{-1}. The reaction products were identified by quantitative mass spectrometry (Hiden HAL/3F) using fragmentation patterns obtained from authentic samples, and they were found to be in good agreement to NIST reference data[34]. Quantitative comparison of the fragmentation patterns of the products of methoxy reactions with formaldehyde and benzaldehyde to authentic samples of methyl formate and benzoic acid methyl ester unambiguously identified these as the main products (Supplementary Figs S1 and S2 and Supplementary Tables S1 and S2). The fragmentation patterns of the other two products were in good agreement with data from the NIST database[34]. No other products were observed in a survey of a wide mass range: m/z 2–200 for benzeneacetaldehyde, m/z 2–150 for benzaldehyde, and m/z 2–100 for acetaldehyde. In all cases, the parent ions of the esters (Fig. 1) were the ions with the highest m/z.

We eliminated the possibility of methanol self-coupling in the cross-coupling reactions by monitoring the 60 amu (methyl formate-d_0) and 64 amu (methyl formate-d_4) signals when using normal methanol and methanol-d_3, respectively.

The CO_2 yield in the cross-coupling between methanol and formaldehyde or acetaldehyde was calculated using the integrated peak area of m/z 44 in the temperature-programmed reaction spectra (corrected for cracking fraction). Importantly, there is no residual carbon after heating to 750 K for these two reactions. In the cases of benzaldehyde and benzeneacetaldehyde, there is a significant amount of residual carbon deposited after reaction with methanol because of the deficiency of oxygen on the surface. The amount of residual carbon was determined by exposing the surface after initial reaction to O_3 followed by heating to react off the carbon as CO_2. The CO_2 yields used to estimate selectivity include CO_2 produced from oxidation of residual carbon.

The relative selectivity towards esters (versus combustion) formed in the self-coupling of methanol and cross-coupling between methanol and aldehydes was estimated on a per aldehyde molecule basis. It was calculated using the ratio of the integrated area of the parent ion of the ester in the temperature-programmed reaction spectroscopy (for example m/z 60 for methyl formate, corrected for cracking fraction) to that of CO_2 (m/z 44, corrected for cracking fraction) divided by the number of carbon atoms in the aldehyde involved in the self- and cross-coupling reactions (divided by 1, 1, 2, 7 and 8 in the self-coupling of methanol and cross-coupling of methanol with formaldehyde, acetaldehyde, benzaldehyde and benzeneacetaldehyde, respectively). Activation energies were estimated using Redhead analysis, assuming a pseudo-first order process and a preexponential factor of 10^{13} s^{-1}. The estimated activation barrier, depending on whether the ester is reaction limited or desorption limited, indicates the reaction barrier or desorption barrier.

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Author contributions

B.X., X.L., J.H. and C.F. conceived and designed experiments, analysed and discussed results, and commented on the manuscript. B.X. performed the experiments and analysed data. B.X. and C.F. co-wrote the paper.

Additional information

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